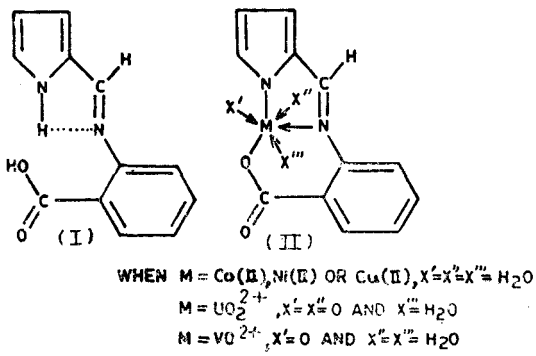

at 670 and 600 cm^{-1} in the metal chelates suggests the formation of M-O and M-N bonds in them. All the chelates indicate one broad band at 3320 cm^{-1} due to νOH of water molecules present. The loss of water molecule at relatively high temperature (>170°) indicates that these are coordinated and not lattice-held.

It appears that due to steric factors 1:2 chelates are not formed. Thus, in view of the magnetic moment, electronic and IR spectral data, Co(II), Ni(II), Cu(II), UO_2^{2+} and VO^{2+} chelates may be assigned octahedral structures (II). The Zn(II) and Cd(II) chelates are tetrahedral as they possess 1:1 (metal-ligand) stoichiometry besides a water molecule.

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Complexes of Dioxouranium(VI) with Bidentate Schiff Bases Derived from Salicylaldehyde & Substituted Anilines

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A series of dioxouranium(VI) complexes of the type $UO_2L_2X_2$ where L=bidentate Schiff base derived from *p*-toluidine, *p*-anisidine, *o*-phenetidine, *o*- or *p*-chloroaniline and X=Cl^-, I^-, NCS^-, NO_3^-, or $\frac{1}{2}SO_4^{2-}$ have been prepared. Analytical, conductance and spectral data have been utilized to characterize the compounds.

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THE present work describes the preparation and characterization of a number of new uranyl complexes with the Schiff bases derived from salicylaldehyde and *p*-toluidine, *p*-anisidine, *p*-phenetidine, *o*- or *p*-chloroaniline.

Hydrated dioxouranium(VI) chloride, nitrate and sulphate (BDH) were used as such. *p*-Toluidine, *p*-anisidine, *p*-phenetidine and *o*-chloro- and *p*-chloroanilines were BDH reagent grade samples. Acetone solutions of dioxouranium(VI) iodide[1] and thiocyanate[2] were obtained by metathesis of dioxouranium(VI) nitrate and sodium iodide or potassium thiocyanate respectively, and filtering the insoluble alkali metal nitrate. The Schiff base ligands were prepared by refluxing an ethanolic solution of the primary aromatic amine and salicylaldehyde in the presence of traces of piperidine for 30 min. Cooling to room temperature gave the solid products which were recrystallized from ethanol and dried *in vacuo*. The purity of these compounds was established by C, H and N analyses.

The chloro, iodo, thiocyanato and nitrato complexes were prepared by reacting stoichiometric quantities (1:2) of the metal salts and the ligand in warm acetone. In some cases stirring and refluxing was necessary. The compounds were suction-filtered, washed with minimum acetone and dried *in vacuo*.

The sulphato complexes were similarly prepared using methanol instead of acetone.

Uranium was estimated as U_3O_8 (ref. 3) following pyrolysis of the diuranate precipitated by aqueous ammonia from a solution of the complex in water. Chloride was estimated as AgCl by precipitation with $AgNO_3$ either as such or after fusion with NaOH and Na_2O_2.

All the present complexes are intensely coloured and are stable in air. They have high melting points and are only sparingly soluble in common organic solvents. The analytical data (Table 1) indicate that 1:2 complexes are obtained in all the cases giving a series of complexes of the type $UO_2L_2X_2$ (L = Schiff base; X = Cl^-, I^-, NCS^-, ONO_2^-, 0·5 SO_4^{2-}).

Except the iodo and thiocyanato complexes (Λ_M = 83-117 ohm^{-1} cm^2 $mole^{-1}$) all the present complexes behave as non-electrolytes in acetone ($10^{-3}M$ solutions). These complexes and the nitrato complexes behave as 1:2 electrolytes in DMF (Λ_M = 104-172 ohm^{-1} cm^2 $mole^{-1}$). Rest of the complexes are non-electrolytes. However, the nitrato complexes act as non-electrolytes in nitromethane. Their 1:2 behaviour in DMF may be due to replacement of coordinated anions by DMF molecules.

The IR spectra of the ligands and the complexes were obtained in mull in the region 4000-500 cm^{-1} on a Perkin-Elmer 337 instrument. The Schiff base ligands and their complexes exhibit νC=N in the range 1620-1640 cm^{-1} and νC=C in the region 1590-1610 cm^{-1}. The phenyl ring vibrations appear in the region 1490-1530 cm^{-1}. The free ligands and the complexes exhibit broad and weak absorption bands in the region 3100-3300 cm^{-1} due to the νOH (ref. 4), and at about 1280 cm^{-1} due to the δOH. Thus, these ligands coordinate to uranyl not as deprotonated anions, but as the neutral ligands similar to some other Schiff base complexes

TABLE 1 — ANALYTICAL AND MELTING POINT DATA OF DIOXOURANIUM(VI) COMPLEXES

Compound	Colour	m.p. (°C)	Found (calc.), %			
			U	C	H	N
UO_2(H-Sal-Tol)$_2Cl_2$	Light yellow	>260	30·4 (31·1)	44·0 (44·0)	3·5 (3·4)	4·1 (3·7)
UO_2(H-Sal-Anis)$_2Cl_2$	Yellow	>260	29·7 (29·9)	42·1 (42·2)	3·5 (3·3)	4·0 (3·5)
UO_2(H-Sal-Phen)$_2Cl_2$	Light yellow	>260	28·4 (28·9)	42·9 (43·7)	3·7 (3·7)	3·8 (3·4)
UO_2(H-Sal-*o*-ClAn)$_2Cl_2$	do	>260	29·1 (29·6)	38·4 (38·8)	2·8 (2·5)	3·7 (3·5)
UO_2(H-Sal-*p*-ClAn)$_2Cl_2$	do	>260	29·4 (29·6)	38·9 (38·8)	2·5 (2·6)	3·4 (3·5)
UO_2(H-Sal-Tol)$_2I_2$	Yellow	>260	24·9 (25·1)	36·2 (35·5)	2·9(2·7)	3·2 (2·9)
UO_2(H-Sal-Anis)$_2I_2$	Orange yellow	245(d)	24·2 (24·3)	34·9 (34·4)	2·7 (2·6)	3·0 (2·8)
UO_2(H-Sal-Phen)$_2I_2$	do	>260	23·5 (23·6)	36·0 (35·8)	3·3 (3·0)	3·3 (2·8)
UO_2(H-Sal-*p*-ClAn)$_2I_2$	Yellow	>240	24·1 (24·1)	31·9 (31·6)	2·4 (2·0)	2·9 (2·8)
UO_2(H-Sal-Tol)$_2$(NCS)$_2$	do	240(d)	29·8 (29·5)	42·0 (41·8)	3·3 (3·2)	7·1 (6·9)
UO_2(H-Sal-Anis)$_2$(NCS)$_2$	do	247(d)	28·2 (27·7)	43·2 (42·8)	3·4 (3·1)	7·1 (6·6)
UO_2(H-Sal-*o*-ClAn)$_2$(NCS)$_2$	do	>240	27·6 (28·0)	39·0 (39·6)	2·6 (2·3)	6·8 (6·6)
UO_2(H-Sal-Tol)$_2$(NO$_3$)$_2$	Orange yellow	235(d)	28·5 (29·1)	41·5 (41·1)	3·2 (3·1)	6·8 (6·9)
UO_2(H-Sal-Anis)$_2$(NO$_3$)$_2$	do	245(d)	27·9 (28·1)	40·2 (39·6)	3·3 (3·0)	6·7 (6·6)
UO_2(H-Sal-Phen)$_2$(NO$_3$)$_2$	Bright yellow	245(d)	27·1 (27·1)	41·6 (41·1)	3·5 (3·4)	6·3 (6·4)
UO_2(H-Sal-*o*-ClAn)$_2$(NO$_3$)$_2$	Yellow	235(d)	28·0 (27·8)	36·5 (36·4)	2·7 (2·3)	6.4 (6·5)
UO_2(H-Sal-*p*-ClAn)$_2$(NO$_3$)$_2$	do	230(d)	27·4 (27·8)	36·8 (36·4)	2·5 (2·3)	6·6 (6·5)
UO_2(H-Sal-Tol)$_2SO_4$	do	235(d)	29·3 (30·2)	42·3 (42·6)	3·5 (3·3)	3·8 (3·5)
UO_2(H-Sal-Anis)$_2SO_4$	do	237(d)	29·2 (29·0)	41·6 (41·0)	3·7 (3·2)	3·3 (3·4)
UO_2(H-Sal-Phen)$_2SO_4$	Orange	235(d)	27·9 (28·1)	42·0 (42·4)	3·4 (3·5)	3·6 (3·3)

H-Sal-Tol, H-Sal-Anis, H-Sal-Phen, H-Sal-*o*-ClAn and H-Sal-*p*-ClAn refer respectively to the Schiff bases derived from salicylaldehyde and *p*-toluidine, *p*-anisidine, *p*-phenetidine, *o*-chloroaniline or *p*-chloroaniline.

of uranium[5]. The IR spectra of all the complexes show an intense band around 920 cm^{-1} attributable to the $\nu_{as}UO_2$ mode. The ν_sUO_2 mode in these complexes appears as a weak band around 790 cm^{-1} and in some cases it was not observed. The observation of this IR band for O=U=O stretching vibrations is consistent with the frequency range observed in other known dioxouranium(VI) complexes[6].

In the thiocyanato complexes reported here $\nu C{\equiv}N$ appeared around 2040 cm^{-1} and $\nu C{-}S$ around 820 cm^{-1} indicating the presence of N-bonded isothiocyanate group[7]. This is in agreement with our expectation, since uranyl ion is known to be a fairly hard acid and should bond to harder N-end rather than the softer S-end[8]. The nitrato complexes studied here do not exhibit any strong absorption in the region 1350-1400 cm^{-1} indicating the absence of uncoordinated nitrate ions, but exhibit strong bands around 1470 and 1270 cm^{-1} assignable to the ν_1(NO stretch) and ν_4(NO_2 asym. stretch) vibrations of the nitrate group respectively. The other nitrate frequencies were observed around 1030, 815, 740 and 718 cm^{-1} in the nitrato complexes, indicating the presence of unidentate[9] nitrate groups. The presence of a bidentate sulphate group (C_{2v}) in the sulphate complexes is evident from the splitting of ν_3 and ν_4 modes and from the appearance at 1000 cm^{-1} of the ν_1 mode which is IR-forbidden in ionic sulphate[10]. It is thus shown on the basis of IR data and molar conductivity values that the neutral bidentate ligand does not displace the sulphato group from the coordination sphere. The presence of bidentate sulphate group in the present complexes gives rise to a four-membered chelate ring structure for the uranyl complex and this is similar to those encountered earlier with bidentate oxygen donors.

The electronic spectra of the complexes (recorded on a Beckman DU 2 instrument) in acetone, DMF, pyridine and nujol mull were found to be remarkably similar. It has been shown[11,12] that the uranyl complexes invariably exhibit band systems characterized by a well-defined vibronic structure between 340 and 500 nm and equatorial ligation has only a minor influence on the spectrum. In all the present compounds, bands in the region 350, 380, 440 and 475 nm were observed. However, the typical band of the UO_2^{2+} group, expected around 390-450 nm, seems to be overlapped by the fairly strong ligand to metal charge-transfer bands[13-15]. This charge-transfer transition probably occurs from the π-orbitals of the Schiff base to the *f*-orbitals of the uranium.

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Si(IV) Complexes with Schiff Bases

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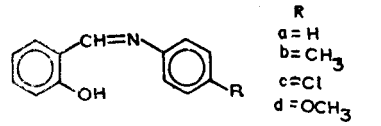
Schiff bases derived from salicylaldehyde and aniline, *p*-toluidine, *p*-chloroaniline and *p*-anisidine react with silicon(IV) chloride in dry benzene medium to form the adducts of the type $(SB)_4SiCl_4$, whereas the Schiff bases derived from salicylaldehyde and *o*-vanillin with *p*-aminodiphenylamine form the adducts of the type $(SB')_2SiCl_4$. These hygroscopic, coloured adducts behave as non-electrolytes in acetonitrile. The infrared spectral study reveals that coordination has taken place through the azomethine nitrogen. It appears that silicon exhibits coordination number eight in $(SB)_4SiCl_4$ type of complexes and six in $(SB')_2SiCl_4$.

THE vast amount of literature added to the growth of understanding the nature of silicon-nitrogen bonds in the complexes of silicon(IV) is mainly due to Wannagat and coworkers[1]. Recently, Paul and coworkers[2] have reported a few Si(IV) complexes with nitrogen donor ligands. However, the limited literature known on silicon(IV) Schiff base complexes[3] has prompted us to undertake a systematic study of silicon(IV) complexes with Schiff bases of types (I) and (II) derived from salicylaldehyde and aniline (Ia), *p*-toluidine (Ib), *p*-chloroaniline (Ic) and *p*-anisidine (Id) and *p*-aminodiphenylamine (IIa) and *o*-vanillin and *p*-aminodiphenylamine (IIb).



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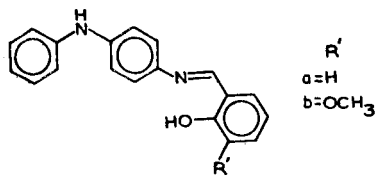

II

The Schiff bases were prepared from reagent grade chemicals according to the method reported elsewhere[4] and dried *in vacuo* over phosphorous pentoxide before use.

All the manipulations were done in a partially evacuated dry-box under oxygen-free nitrogen.

The complexes were prepared as follows: A solution of silicon tetrachloride super dry benzene[5] was treated with a slight excess of Schiff base dissolved in the same solvent and left for several hours with occasional shaking at room temperature. Sufficient time was allowed for the precipitate to settle. The complex was filtered, washed free from the reagent with benzene and dried *in vacuo* over fused calcium chloride.

The data in Table 1 show that silicon tetrachloride forms adducts with all the Schiff bases employed. The Schiff bases Ia-d form adducts of 1:4 stoichiometry whereas IIa and IIb form adducts of 1:2 stoichiometry. All these adducts are dark coloured, hygroscopic substances, soluble in acetonitrile, DMF and DMSO. These undergo hydrolysis readily in water.

The molar conductance values in purified acetonitrile[5] (concentration $10^{-3}M$) fall in the range 31-62 ohm^{-1} cm^2/mole, indicating non-electrolyte nature of the complexes in acetonitrile. Molar conductance of 1:1 electrolyte in acetonitrile[6] falls in the range 190-195 ohm^{-1} cm^2/mole. The low conductance observed may be due to the partial solvolysis of the complexes in acetonitrile.

Some adducts with *o*-hydroxyazomethines are documented in the literature, especially with Sn(IV), Ti(IV) and Si(IV). In view of these evidences it may be considered that presently synthesized complexes are also adducts, and not substitution complexes involving *o*-hydroxy group of the Schiff bases in which case a molecule of hydrogen chloride liberated would have attached with azomethene nitrogen to give 1:1 electrolytes. Further support to this conjecture is provided by the IR data in nujol.

The broad weak bands in the Schiff bases in the region 2800-2600 cm^{-1} are retained in the corresponding complexes. The coordination through nitrogen should either weaken the strength of H-bonding or allow the formation of H-bonding with the π-system of the azomethine group. The bond due to phenolic C—O in the region 1289-1272 cm^{-1} in the Schiff bases does not show any shift towards the higher frequency region in the complexes. These observations suggest that the *o*-hydroxy group of the Schiff bases Ia-d and IIa, b, is not involved in the bond formation.

TABLE 1 — PHYSICAL PROPERTIES AND ANALYSIS OF SILICON(IV) SCHIFF BASE COMPLEXES
[Silicon estimated as SiO_2]

Sl No.	Empirical formula	Si(%)		N(%)		Cl(%)		Colour
		Found	Calc.	Found	Calc.	Found	Calc.	
1	$(C_{13}H_{11}NO)_4SiCl_4$	2·91	2·92	5·24	5·85	14·80	14·82	Orange
2	$(C_{14}H_{13}NO)_4SiCl_4$	2·88	2·76	5·56	5·52	14·00	14·01	do
3	$(C_{13}H_{10}NOCl)_4SiCl_4$	2·56	2·56	5·29	5·12	12·89	12·98	Yellowish green
4	$(C_{14}H_{13}NO_2)_4SiCl_4$	2·77	2·60	5·38	5·19	12·64	12·17	do
5	$(C_{19}H_{16}N_2O)_2SiCl_4$	3·66	3·70	7·48	7·41	18·86	19·04	Brownish black
6	$(C_{20}H_{18}N_2O_2)_2SiCl_4$	3·72	3·47	6·86	6·95	17·50	17·62	do

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